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US-A- 3 567 453
US-A- 3 793 033
US-A- 4 247 611

PHOTOGRAPHIC SCIENCE AND ENGINEERING, vol.16, no. 4, July-August 1972, pages 300-312, Washington, D.C., US; D.G. BORDEN: "Review of light-sensitive tetraaryborates"

PHOTOGRAPHIC SCIENCE AND ENGINEERING, vol. 23, no. 3, 5th June 1979, pages 140-143, Society of Photographic Scientists and Engineers, Washington, D.C., US; S.P. PAPPAS et al.: "Photoinitiated cationic polymerization by photosensitization of onium salts"

J. VAC. SCI. TECHNOL., vol.19, no. 4, November/December 1981, pages 1111-1116, American Vacuum Society; S.R. FAHRENHOLTZ: "Novolac resins as active ingredients in positive electron resists"

IBM TECHNICAL DISCLOSURE BULLETIN, vol. 23, no. 9, February 1981, page 4290, New York, US; E. GIPSTEIN et al.: "Synthesis of novolak p-cresol-formaldehyde resins for deep UV lithography"

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Description

This invention relates to a radiation-sensitive composition of particular utility in both positive and negative-acting printing plates.

5 A positive-acting printing plate comprises a radiation-sensitive coating which, after exposure to the appropriate wavelength light, becomes more soluble in developer than non-exposed areas. In practice, the vast majority of coatings which undergo photosolubilisation upon exposure consist of quinone diazides, commonly known as diazo oxides, together with phenolic resins. Diazo or diazonium photosensitive coatings are primarily sensitive to actinic light of a wavelength between 350 nm to 410 nm; by the addition of various
10 additives the sensitivity can be increased to 550 nm. United States Patent Specification No. 4 248 959 discloses the sensitisation of negative-acting compositions which utilise diazonium salts and reports that positive-acting quinone diazide systems do not exhibit the ability to be dye sensitised for use with visible laser radiation.

The ability to produce a direct laser addressable plate is an ever increasing market need, as more and
15 more images for photographic transferral to printing plates are being arranged and even generated by computer. These images include computer generated characters for photo-typesetting, computerised copy editing and justification, and computerised scanning and halftone "screening" of continuous tone pictures. These images may first appear in "soft" form, e.g. on a cathode ray tube, and then be made into a "hard" copy, for example a photographic transparency to be used as a light mask. Eliminating the need of the
20 transparency and being able to go direct to the plate has the advantage of removing a complete stage in the process, with the associated savings in time, errors and expense.

Visible or infrared laser radiation has been used to perform mechanical or thermal work such as melting, vapourising or ablating, to form a printing plate. However, all uses of the laser which involve imaging by means of ablation, instead of photohardening or photosolubilisation, are economically inferior
25 because of high power requirements and attendant cooling costs.

In contrast to quinone diazides and diazonium salts which can only be poorly sensitised, if at all, onium salts are very readily sensitised by wide classes of compounds covering the whole of the visible and infrared regions of the electromagnetic spectrum.

Onium salts have been utilised as initiators in the polymerisation of cationically polymerisable materials.
30 British Patent Application Publication Nos. 2 061 280A, 2 042 550A, 2 027 435A, 2 013 208, United States Patent Specification Nos. 4 250 053 and 4 026 705, and European Patent Application Publication Nos. 54509, 44274 and 35969 disclose cationically polymerisable compositions including onium salts such as diaryliodonium salts, aromatic onium salts, triarylsulphonium salts, aromatic sulphonyl sulfoxonium salts and carbamoyl sulfoxonium salts. The compounds disclosed may be polymerised upon exposure to
35 radiation and/or heating to provide hard tack-free resistant materials.

A method of preparing photosolubilising coatings is disclosed in United States Patent Specification No. 4 247 611. Organic polymeric compounds with recurrent acetal or ketal groups in the main chain are utilised whose solubility in a liquid developer is increased by the action of acid. The acid is generated in exposed areas by the action of actinic radiation on acid releasing molecules. Phenolic resins are disclosed
40 as optional alkali-soluble binders for incorporation in addition to the photosolubilisable polyacetal or polyketal.

U.S. Patent No. 3,567,453 discloses radiation sensitive compounds comprising a tetrasubstituted borate anion and an organic cation containing an atom selected from the group consisting of nitrogen, arsenic, tin, antimony, sulfur, iodine, phosphorus, oxygen, titanium, palladium, chromium and cobalt. These compounds
45 can be spectrally sensitised and can be used in photoresists and for lithography. In certain system, an alkali soluble phenol formaldehyde resin is used which forms a reaction product with a radiation sensitive compound which is insoluble in alkali but which forms decomposition products upon exposure to actinic rays which are soluble in dilute alkali.

It has been found that there is an interaction between alkali-soluble phenolic resins and certain onium salts which results in a solvent resistance, more particularly an alkali solvent resistance, to the composition when it is cast into a film. Furthermore, the photolytic decomposition of the onium salt restores solubility to the resin, thus fulfilling the basic requirements of a photosolubilising system. The presence of an organo borate salt is not required. Onium salts can be sensitised to a wide range of the electromagnetic spectrum from the UV through the visible and into the infrared.

55 Th refor according to the pr sent invention there is provided a radiation-sensitive composition comprising an alkali-soluble phenolic resin and a radiation-sensitive onium salt, the composition being photosolubilisable and the onium salt being selected from a rang of salts defined hereinafter.

According to a further aspect of the invention there is provided a radiation-sensitiv element comprising

a layer of a composition of the invention coated on a substrate.

Phenolic resins which are used in this invention are those which are alkali-soluble, i.e. they contain sufficient phenolic OH groups to render the polymer soluble in aqueous alkali. This solubility is such that a phenolic resin coating in the absence of onium salt, would be removable by mild rubbing and soaking in 2% aqueous sodium metasilicate pentahydrate at 20°C within 20 minutes. Thus, the solubility is sufficient to enable a film of the polymer to be removed from a substrate during the development stage.

It has been found that when an onium salt is mixed with an alkali-soluble phenolic resin it imparts a solvent resistance to the resin with respect to aqueous alkali solvents. This solvent resistance is reduced upon irradiation thereby providing a differential solubility between exposed and non-exposed areas of such phenolic resin/onium compositions. The photosolubilisable property of the phenolic resin/onium compositions can provide the basis of an imaging system, e.g. for the production of printing plates.

The radiation-sensitive elements or compositions of the invention possess properties which are completely different from those of the prior art compositions comprising onium salts. Whilst certain of the prior art references referred to above disclose compositions comprising polymerisable phenolic resin and an onium salt, the prior art compositions are polymerised upon exposure to radiation and/or heat whereas the compositions of the invention are not polymerised upon exposure to radiation but are transformed from a relatively alkali-insoluble state to an alkali-soluble state upon exposure to radiation. It appears that many of the specific phenolic resins used in the prior art were modified with functional groups, e.g. epoxy, vinyl and allyl, to allow free radical or cationic polymerisation. These functionalities were bonded either directly onto the aromatic nucleus or indirectly through the oxygen linkage. In the latter case, alkali-solubility of the resin would be significantly decreased. In general, the onium salts are used in catalytic amounts of up to 4% by weight of polymerisable material, usually up to 2%. Furthermore, most of the compositions of the prior art tended to be oils or gums whereas in general those of the subject invention are in the form of non-tacky solids.

The compositions of the invention comprise two essential components, namely a phenolic resin and an onium salt, both of which components are readily available. The compositions are simple and effective for use in the production of printing plates and do not require the presence of specialised polymers, e.g. polymers containing acetal or ketal groupings, as are often required in the photosolubilising systems of the prior art.

The composition comprising alkali-soluble resin and photosolubiliser is initially alkali-insoluble and upon irradiation the onium salts decompose restoring the original solubility of the resin, thus rendering the composition alkali-soluble. In order to ensure alkali-solubility of the composition upon irradiation, the composition must be substantially free from functional groups which would polymerise/cross-link in the presence of onium salts upon irradiation. Thus, the phenolic resin should not be heavily modified with functional groups, e.g. epoxy, vinyl and allyl groups, which would cross-link or polymerise in the presence of onium salts upon irradiation leading to permanent insolubilisation of the resin. Furthermore, such functional groups should not be present in the composition in the form of additional components, e.g. monomers, binder, etc. Thus, the phenolic resins used in the invention are non-polymerisable although they are capable of being cross-linked upon heating by a reaction involving the elimination of water.

Whilst the phenolic resins have been classified herein in relation to their alkali-solubility, it will readily be appreciated that other solvent systems may be used in place of an aqueous alkali developer in the preparation of printing plates. In certain cases the differential solubility between exposed and unexposed compositions may be enhanced in relation to solvent systems other than aqueous alkali, e.g. aqueous organic solvent mixtures such as methanol or acetone and water mixtures.

The phenolic resins useful in this invention are the condensation products from the interaction between phenol, C-alkyl substituted phenols (including cresols, xlenols, p-tert-butyl-phenol, p-phenylphenol and nonyl phenols), diphenols, e.g. bisphenol-A (2,2-bis(4-hydroxyphenyl)propane), and aldehydes such as formaldehyde, acetaldehyde, chloral and furfuraldehyde. The type of catalyst and the molar ratio of the reactants used in the preparation of phenolic resins determines their molecular structure and therefore the physical properties of the resin. An aldehyde:phenol ratio between 0.5:1 and 0.1:1 usually 0.5:1 to 0.8:1, and an acid catalyst is used to prepare those phenolic resins generally known as novolacs which are thermoplastic in character. Higher aldehyde:phenol ratios of more than 1:1 to 3:1, and a basic catalyst give rise to a class of phenolic resins known as resoles, and these are characterised by their ability to be thermally hardened at elevated temperatures. Both these classes of phenolic resin, novolacs and resoles, are useful in this invention. Examples of the resins used in this invention are BKR 2620 from Bakelite Xylonite Ltd., and Aroclene 24780 from Ashland Chemicals which are resoles, and CRJ 406 from Schenectady Chemicals Inc. and Reichhold 29802 from Reichhold Chemicals Inc. which are novolacs.

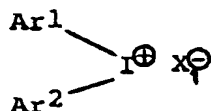
In addition to the resin, there is required a photosolubiliser which is an onium salt selected from

iodonium, sulphonium, oxysulphonium, sulphoxonium, salts which are defined hereinafter. Preferably, an iodonium, sulphonium or oxysulphonium is present, most preferably it is an iodonium salt since it is the most photosensitive and also the easiest to spectrally sensitise.

The onium salt is generally included in the composition in an amount in the range from 1 to 40% by weight of the total weight of phenolic resin and onium salt. The amount of onium salt is selected to provide the desired solubility differential between the unexposed and exposed compositions. It has been found that resole resins normally require the onium salt in an amount of at least 5% by weight of the total weight of phenolic resin and onium salt in order to ensure a satisfactory solubility differential. Generally, compositions employing resole resins will include at least 7% by weight of onium salt. It is possible to achieve a satisfactory solubility differential in compositions containing novolac resins containing smaller amounts of onium salt, generally in the range 1 to 40% by weight of onium salt.

Iodonium salts are compounds having a positively charged iodine atom bearing two covalently bonded carbon atoms and any anion. Aliphatic iodonium salts are not normally thermally stable at temperatures above 0°C. However, stabilised alkyl phenyl iodonium salts such as those disclosed in Chem. Lett. 1982, 65-6 are stable at ambient temperatures and may be used in the invention. The preferred compounds are diaryl and aryl-heteroaryl iodonium salts in which the carbon-to-iodine bonds are from aryl or heteroaryl groups.

Iodonium salts for use in the invention represented by the formula:



in which:

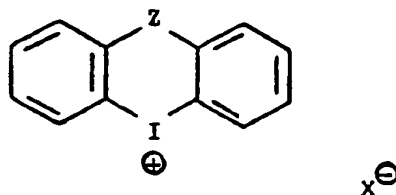
Ar¹ and Ar² independently represent aromatic groups optionally substituted and optionally linked together to include the iodine atom within a ring structure, preferably a heterocyclic aromatic ring, and

X[⊖] represents an anion according to Claim 1.

These aromatic groups generally have from 4 to 20 carbon atoms, may be selected from aromatic hydrocarbon rings, e.g. phenyl or naphthyl and hetero-aromatic groups including thienyl, furanyl and pyrazolyl, and may be substituted with alkyl groups, e.g. methyl, alkoxy groups, e.g. methoxy, chlorine, bromine, iodine, fluorine, carboxy, cyano or nitro groups, or any combinations thereof. Condensed aromatic-heteroaromatic groups, e.g. 3-indoliny, may also be present.

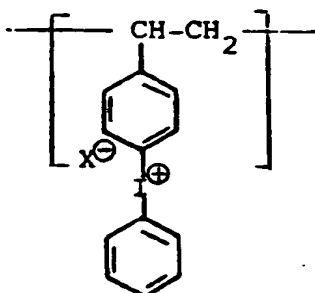
Preferably Ar¹ and Ar² do not have more than two substituents at the α positions of the aryl groups. Most preferably Ar¹ and Ar² are both phenyl groups containing no α substituents.

The α positions of the aryl groups may be linked together to include the iodine atom within a ring structure to give a formula such as:



in which Z is an oxygen or sulphur atom.

Other suitable iodonium salts include polymers containing the monomeric unit:



Any anion appears to be useful as the counter-ion in the onium salt. Preferably the acid from which the anion is derived has a $pK_a < 5$. Suitable inorganic anions include halide anions, HSO_4^- , and halogen-containing complex anions, e.g. tetrafluoroborate, hexafluorophosphate, hexafluoroarsenate and hexafluoroantimonate. Suitable organic anions include those of the formulae:

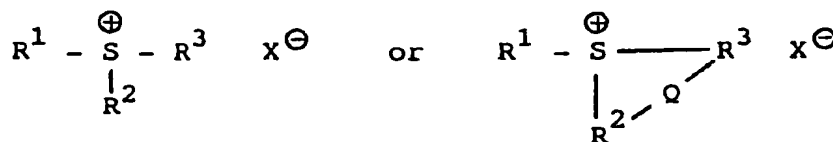


in which R^8 is an alkyl or aryl, e.g. phenyl, group either of which may be substituted. Examples of such anions include CH_3COO^- and CF_3COO^- .

The most significant contribution of the anion is its effect upon the solubility of the onium salt in different solvents or binders.

Sulphonium salts are also useful in this invention as they are photosensitive and can also be spectrally sensitised. As they comprise a positively charged sulphur atom bearing three covalently bonded carbon atoms, they are however more prone to steric hindrance which can limit the extent of interaction between sulphonium salts and phenolic resins.

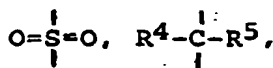
Aromatic sulphonium salts for use in the invention have the following formula



In which:

at least one of R^1 , R^2 and R^3 is an optionally substituted aromatic group which preferably has from 4 to 20 carbon atoms, the remaining groups being selected from optionally substituted aliphatic groups containing up to 12 carbon atoms, preferably up to 6 carbon atoms and aromatic groups as defined above. Preferably R^1 , R^2 and R^3 are each aromatic.

Q is a carbon-to-carbon bond or a linking group selected from O , S , $>S=O$, $>C=O$,



or $>N-R^5$, in which

R^4 and R^5 are independently selected from hydrogen, an alkyl group having from 1 to 4 carbon atoms, and an alkenyl group having from 2 to 4 carbon atoms,

R^6 is an aryl group having from 6 to 20 carbon atoms, such as phenyl, or an acyl group having from 2 to 20 carbon atoms, such as acetyl or benzoyl, and

X^- is an anion.

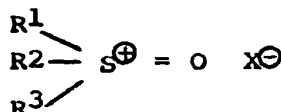
Aromatic sulphonium salts are known and recognised in the art. Triaryl-substituted sulphonium compounds, for example, can be prepared by the procedures described in C.H. Wiggand et al, "Synthesis and Reactions of Triarylsulphonium Halides", J. Org. Chem. 33, 2671-75 (1968). Aromatic sulphonium salts also having alkyl substitution can be prepared by the procedures described in K. Ohkubo et al, J. Org. Chem.

36, 3149-55 (1971). The preferred method for making triaryl-substituted sulphonium compounds is described in United States Patent Specification No. 2 807 648 from which complex sulphonium salts of complex ions can be made. The complex sulphonium salts can be prepared from the corresponding simple salts such as bisulphate or halide salts, by metathesis with a metal or ammonium salt or acid of the complex anion desired.

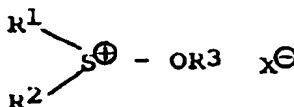
The aromatic groups may be selected from phenyl, thienyl and furanyl groups. The aromatic groups may optionally have one or more fused benzo rings (e.g. naphthyl, benzothienyl, dibenzothienyl, benzofuranyl and dibenzofuranyl). The aromatic groups may also be substituted, if desired, by groups which are essentially non-reactive with other components present in the particular composition in which the salt is to be used, such as halogen, nitro, aryl, ester groups (including alkoxycarbonyl), such as methoxycarbonyl, ethoxycarbonyl and phenoxycarbonyl, and acyloxy (such as acetoxy and propionyloxy), alkoxy groups (such as methoxy, ethoxy and butoxy), aryl groups (such as phenyl), alkyl groups (such as methyl, ethyl and t-butyl), aryloxy groups (such as phenoxy), alkylsulphonyl groups (such as methylsulphonyl and ethylsulphonyl), arylsulphonyl groups (such as phenylsulphonyl), hydrocarbylthio groups (such as p-phenylthio and methylthio) and perfluoroalkylsulphonyl groups (such as trifluoromethylsulphonyl and perfluoro-butylsulphonyl).

Of the aromatic sulphonium complex salts, the preferred salts are the triaryl-substituted salts such as triphenylsulphonium hexafluorophosphate. The triaryl-substituted salts are preferred because they are more thermally stable than the mono- and diaryl-substituted salts and are more amenable to dye sensitisation.

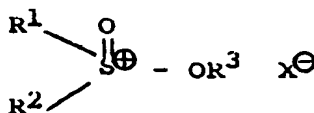
The following sulphonium salts containing oxygen-sulphur linkages may be used in this invention. sulfoxonium salts of the general structure.



as disclosed in United States Patent Specification Nos 4 339 567, 4 383 025 and 4 398 014, oxysulphonium salts of the general formula.



as disclosed by C.R. Johnson and W.G. Phillips in J. Org. Chem. Vol. 32, 1967 (1926), and oxysulphoxonium salts of the general formula.



as disclosed by G.R. Chalkley et al. in J. Chem. Soc. (C) 1970, p. 682,

in which R¹ to R³ are as defined above, with the exception that each of R¹ to R³ may represent optionally substituted aliphatic groups.

The maximum sensitivity of the binary mixtures of the invention is generally in the ultraviolet region. However, the sensitivity of the mixtures can readily be adjusted by the addition of one or more spectral sensitizers. Suitable spectral sensitizers are well known in the art and cover the full spectral range from UV to infrared (280 to 1100 nm). Normal sources for exposure of photosensitive lithographic plates are designed to emit ultraviolet light to match the sensitivity of commercially available plates. However, the light sources often also emit visible light to which prior art plates are insensitive. The compositions of the invention may be sensitized to cover the full spectral range thereby making maximum use of the exposure energy. Additionally, increased sensitivity to UV light may be achieved.

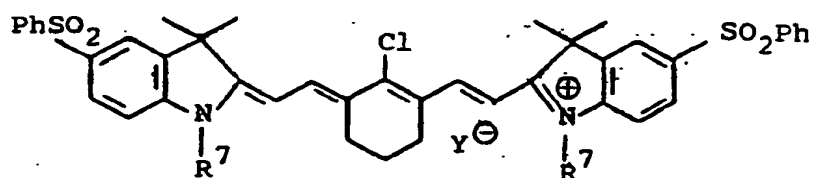
Examples of compounds which are known to sensitize onium salts are those in the following classes:

diphenylmethane including substituted diphenylmethane, such as amino substituted diphenylmethane, xanthene, acridine, methine and polymethine (including oxonol, cyanine and merocyanine) dy, thiazol, thiazine, azine, aminoketone, porphyrin, coloured aromatic polycyclic hydrocarbon, p-substituted aminostyryl compound, aminotriazyl methane, polyarylene, polyarylpolylene, 2,5-diphenylisobenzofuran, 2,5-diarylcyclopentadiene, diarylfuran, diarylthiofuran, diarylpyrrole, polyarylphenylene, coumarin and polyaryl-2-pyrazoline. The addition of a sensitizer to the system renders it sensitive to any radiation falling within the absorption spectrum of the said sensitizer. The efficiency of the irradiation will increase the nearer it coincides with λ_{max} of the sensitizer.

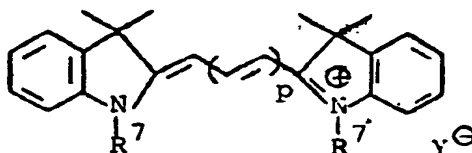
Generally sensitizers of the reactive type, those which are attacked by the photoproducts of exposure, such as oxonol dyes, are incorporated at levels of up to 10% by weight of the total weight of phenolic resin, onium salt and sensitizer. The sensitizer is generally present in an amount of from 5 to 200% molar with respect to the onium salt.

Energy transfer sensitizers which are not attacked by photoproduct would be useful at much lower levels of incorporation, e.g. 0.1 to 5% molar with respect to the onium salt.

Preferably sensitizers are oxonol dyes and cyanine dyes, particularly cyanine dyes of the formula:



or



in which:

R^7 represents an alkyl group of 1 to 6 carbon atoms, e.g. methyl, ethyl, n-butyl, n-hexyl,

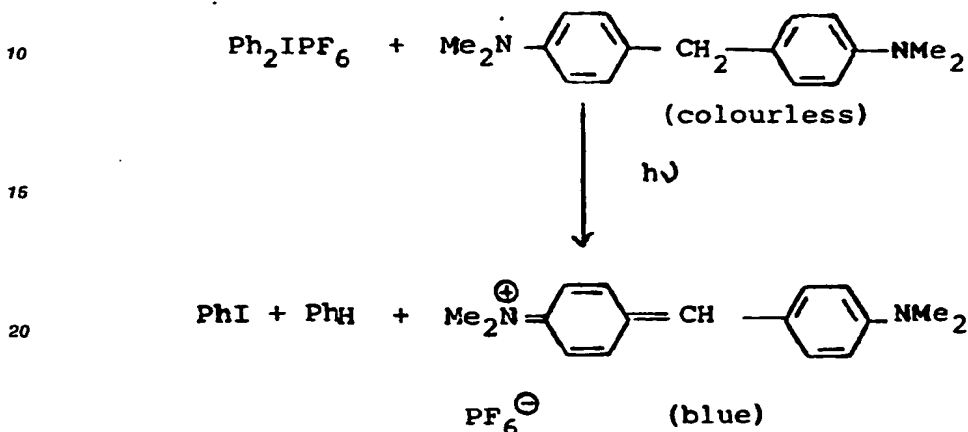
Y^- represents an anion, such as $C_2F_5C_6F_{10}SO_3^-$ (perfluoro(4-ethylcyclohexyl)sulphonate), or ClO_4^- ; and

p is 1 or 2.

While in many cases it is possible to prepare photosolubilising systems from phenolic resins and onium salts, there are some phenolic resins which do not readily revert to an alkali-soluble form after having been irradiated. This is thought to be because in these cases the photolysed onium salt abstracts a hydrogen atom from the resin, which then either dimerises or undergoes further oxidation to form a carbonyl functionality from what originally was a phenolic-OH group. Both of these reactions would cause the resin to decrease its alkali solubility. In these cases, it has been found that the addition of an alternative source of hydrogen atoms such as amines can restore the photosolubilising properties of the system. It has been found that there is an approximately 1:1 molar ratio relationship between onium salts and amines in such systems, as is shown in Figure 1, in which "t" is the time in minutes to dissolve a film of novolac resin containing 15% iodonium salt in 6% aqueous sodium metasilicate pentahydrate and "ratio" is the tributylamine: diphenyliodonium hexafluorophosphate molar ratio. From the Figure it can be seen that the addition of amine to a novolac resin-onium salt system restores the photosolubility markedly up to an equimolar ratio with the onium salt, and any surplus amine has little effect on the degree of photosolubilisation. However, if the amine is soluble in developer, as in the Example shown, it can still affect the solubility of the film in non-irradiated areas. It is, therefore, beneficial not to have a large surplus of a soluble amine as it can reduce the differential in solubility between exposed and non-exposed regions and also can effect the shelf life of the system. A preferred range of the molar ratio is from 0.5:1 to 3:1, most preferably 1:1. The amine content generally comprises up to 25% by weight of the total weight of phenolic resin, onium salt and amine.

One of the requirements for a commercially viable printing plate is that it should exhibit a visible image

at both post-exposure and post-development stages. In the systems which need a hydrogen atom source to render them more easily photosolubilising, it is possible to use compounds which are also the leuco forms of dyes. Upon exposure to light, such systems generate the oxidized form of the dye in exposed areas resulting in a highly coloured visible image. One such useful material is bis(4-dimethylaminophenyl)methane which is essentially colourless, but gives a dense blue image upon oxidation with an iodonium salt. The reaction which is believed to occur is as follows:



25

A further advantage of using compounds such as bis(4-dimethylaminophenyl)methane as additives to the described compositions is that they enhance the solubility differential between exposed and unexposed areas. This is due to the amine initially imparting hydrophobicity to the coating as it is not soluble in the aqueous developer. After exposure the amine is oxidized to an ionic dye which is soluble in developer. Thus, it is possible to prepare photosolubilising coatings which after exposure may quickly and completely dissolve in developer, e.g. 20 seconds, compared to the unexposed areas which only lose approximately 15% of the weight after 180 seconds.

Radiation-sensitive elements in accordance with the invention are prepared by coating a suitable substrate with a layer of a composition of the invention from a suitable solvent. Exemplary substrates include fibre base materials such as paper, polyethylene-coated paper, polypropylene-coated paper, parchment, cloth and the like; sheets and foils of such metals as aluminium, copper, magnesium and zinc; glass and glass coated with such metals as chromium, chromium alloys, steel, silver, gold and platinum; synthetic polymeric materials such as poly(alkyl methacrylates), e.g. poly(methyl methacrylate), polyesters, e.g. poly(ethylene terephthalate), poly(vinylacetals), polyamides, e.g. Nylon, cellulose esters, e.g. cellulose nitrate, cellulose acetate, cellulose acetate propionate, cellulose acetate butyrate, and the like.

Typical lithographic support materials which are useful in the invention include supports such as zinc, anodized aluminium, grained aluminium, copper and specially prepared metal and paper supports; superficially hydrolysed cellulose ester films; polymeric supports such as polyolefins, polyesters, polyamide and the like.

The supports can be sub-coated with known subbing materials such as copolymers and terpolymers of vinylidene chloride with acrylic monomers (such as acrylonitrile and methyl acrylate) and unsaturated dicarboxylic acids (such as itaconic acid or acrylic acid); carboxymethyl cellulose, polyacrylamide; and similar polymeric materials.

The support can also carry a filter or antihalation layer, such as one comprising a dyed polymer layer which absorbs the exposing radiation after it passes through the radiation-sensitive layer and eliminates unwanted reflection from the support. A yellow dye in a polymeric binder, such as one of the polymers referred to above as suitable sub-coatings, is an especially effective antihalation layer when ultraviolet radiation is employed as the exposing radiation.

The radiation-sensitive elements of the invention can be used to produce a positive lithographic image by image-wise exposing the element to actinic radiation and thereafter developing the element with a suitable developer so that the composition is removed in the irradiated areas thereby producing said image. Preferably, the developer is an aqueous alkali-based solution although other developers which preferentially dissolve the irradiated areas may be used.

The radiation-sensitive elements of the invention may also be utilised to produce a negative image in a similar manner to the technique disclosed in British Patent Application Publication No. 2 082 339A.

British Patent Application Publication No. 2 082 339A discloses a light-sensitive composition for coating lithographic plates to provide for positive/negative processing and comprises an orthoquinone diazide and at least one resole resin. In order to obtain a lithographic image from a positive original the lithographic plate is exposed to light through the positive original and thereafter developed with an alkali-based developer so that the coating is removed from the irradiated areas of the plate. A lithographic image from a negative original is obtained by exposing the plate to light through the negative original, heating the plate so as to convert the coating in the irradiated areas to a form insoluble in alkali, thereafter further exposing the plate overall to light so that the areas not previously irradiated are rendered alkali-soluble whereas the areas previously irradiated remain insoluble in alkali and developing the plate with an alkali-based developer so as to remove the coating from those areas of the plate where it is rendered soluble by the further exposure.

The radiation-sensitive elements of the invention may be utilised to produce a negative image by image-wise exposing the element to actinic radiation, heating the element so as to convert the coating in the irradiated areas to a form insoluble to alkali, further exposing the element overall to actinic radiation so that areas not previously exposed are rendered alkali-soluble, and developing the element with a developer so that the coating is removed from those areas of the element rendered soluble by the further exposure thereby producing the image.

After development, the radiation-sensitive elements of the invention may be subjected to a further heat treatment, e.g. at 220°C for about 10 minutes to improve the solvent resistance of the element.

Compositions of the invention may also be used as positive photoresists for the preparation of metal-clad printed circuit boards, e.g. copper sheet laminated to an epoxy resin board. In this instance, the copper would be coated with the photosensitive composition. After exposure the solubilised material would be removed leaving an integral mask. Unprotected areas of copper would then be removed by etching such as with aqueous ferric chloride solution.

The compositions of the invention may also be used to protect other materials such as amorphous SiO₂. Silica is often used in the fabrication of electronic devices and integrated circuitry and the contact patterns for these devices are often defined through photomasks.

The compositions of the invention may contain other ingredients such as stabilising additives, inert colourants, lithographic printing aids, e.g. tung oil, and additional non-reactive polymeric binders. Generally, the total amount of such ingredients does not amount to more than 70% based on the total weight of phenolic resin, onium salt and additional ingredients.

The invention will now be more particularly described with reference to the following Examples.

In the Examples the following commercially available products were used:

35	BKR 2620	a resole type resin commercially available from Bakelite Xylonite Ltd.
	Aroclene 24780	a phenolic resin commercially available from Ashland Chemicals Co.
	CRJ 406	a phenolic resin commercially available from Schenectady Chemicals Inc.
	Multilith	an offset press commercially available from A.M. Multigraphics Ltd.
	Reichhold 29802	a novolac resin commercially available from Reichhold Chemicals Inc.
40	Ascor	an exposure unit commercially available from Berkey Technical
	Waxoline Yellow TS	- a solvent soluble quinoline dye
	Waxoline Rubin	a solvent soluble anthraquinone dye
	Victoria Blue	a water-soluble triarylmethane dye
	Model 299SL	an overhead projector commercially available from Minnesota Mining and Manufacturing Company
45	PL 5000	an exposure unit commercially available from Parker Graphics Ltd.
	No. 4 Wratten filter	- commercially available from Kodak Limited
	FOGRA PMS2	a plate control wedge commercially available from FOGRA Institute, Switzerland
	UGRA/Gretag	a plate control wedge 1982 commercially available from UGRA, Switzerland
50	NuArc platemaker	commercially available from NuArc Company Incorporated, Chicago, U.S.A.

Examples 1 to 4

Method

65

A coating solution was prepared by the following technique. 10 g of phenolic resin BKR 2620 was dissolved in 30 g of butan-2-one.

To 5 g aliquots of the resin solution were added, i.e. 1.25 g resin:

(1) 0.05 g of diphenyliodonium hexafluorophosphate (Ph_2IPF_6),

(2) 0.1 g Ph_2IPF_6 ,

(3) 0.2 g Ph_2IPF_6 ,

(4) 0.4 g Ph_2IPF_6 ,

5 respectively. Using these solutions, coatings were made under subdued lighting conditions, using a No. 3 wire-wound coating bar manufactured by RK Print-Coat Instruments Ltd., and slurry-grained aluminium as the substrate. The coatings were then air dried overnight in the dark and then for 1 minute at 100°C; Samples measuring 15 cm x 8 cm were then exposed by the following means. The samples were placed in vacuum contact with a photographic step wedge comprising 0.15 increments in optical density per step and a 60 lines per cm screen test target in which areas were covered with 3 to 97% dots, made by Colour Service Inc. The UV source was a 5 kW metal halide lamp fitted in a Parker Graphics Ltd. PL 5000 exposure unit. The samples were irradiated by 25 units (about 70 seconds) at a distance of 0.7 m. The exposed areas were slightly pink in colour and upon immersion in developer solution, which was 6% aqueous sodium metasilicate pentahydrate, preferentially dissolved leaving a high quality positive image of hydrophobic phenolic resin on a hydrophilic aluminium substrate. The results are given in Table 1.

Table 1

Example No.	Weight % of iodonium based on resin	Time in developer to give 2 to 3 clear steps
1	4	20 seconds
2	8	80 seconds
3	16	200 seconds
4	32	500 seconds

The above experiments show that coatings containing higher levels of iodonium salts are slower to solubilise than coatings containing lower levels of iodonium salts. This is as would be expected because the more of the insolubilising iodonium salt present in a coating, the more resistant to alkali the coating would be and more iodonium salt needs to be photolytically decomposed. Consequently, there is an optimum level for iodonium salt concentration in each resin to achieve the best balance between rate of photosolubilisation and the greatest differential between exposed and non-exposed areas with respect to alkali resistance.

Examples 5 to 8

Method

A coating solution was prepared by the following technique. 10 g of a phenolic resin Aroclene 24780 was dissolved in 30 g of butan-2-one. To 5 g aliquots of this solution was added:

(5) 0.05 g Ph_2IPF_6

(6) 0.1 g Ph_2IPF_6

(7) 0.2 g Ph_2IPF_6

(8) 0.4 g Ph_2IPF_6

55 respectively. Using these solutions, coatings were made on an aluminium substrate with a No. 3 wire-wound coating bar. These coatings were dried immediately at 85°C for 2 minutes. Exposures were made using the same test targets and exposure source as described in Examples 1 to 4. The source was positioned 0.7 m from the test samples and they were irradiated for 25 units. The results are given in Table 2.

Table 2

Example No.	% iodonium based on resin	No. of steps clear after 40 second development
5	4	*
6	8	5
7	16	3
8	32	1

* After 20 seconds in 6% developer there was substantial coating weight loss in non-exposed areas.

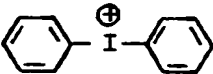
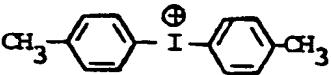
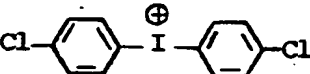
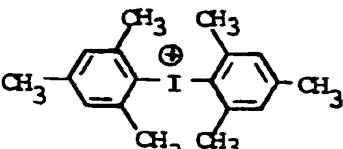
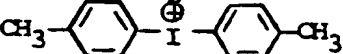
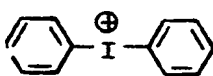
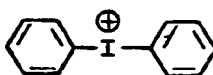
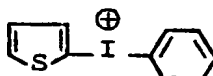
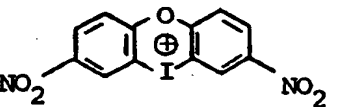
A similar trend was observed in these Examples, which used Arofene 24780 as the resin, as was seen in Examples 1 to 4 which used BKR 2620 as the resin. If the percentage of iodonium ion in the resin falls too low, then the coating does not have sufficient resistance to alkali attack. If the iodonium level is too high, then the photosolubilisation process becomes too slow to have a practical use.

Examples 9 to 17

The following series of Examples demonstrate the range of iodonium salts which have been found to be useful in the present invention.

The experimental method consisted of taking 5 g of 25% w/w Arofene 24780 in butan-2-one and adding to it the quantities of the iodonium salts shown in the following Table 3.

Table 3

Example	Iodonium cation	Anion	Quantity
9		PF ₆	0.21 g
10		PF ₆	0.23 g
11		PF ₆	0.25 g
12		PF ₆	0.23 g
13		Cl	0.2 g
14		Br*	0.2 g
15		SbF ₆	0.2 g
16		CF ₃ CO ₂	0.2 g
17		PF ₆	0.13 g

* Insufficiently soluble to evaluate

All samples were exposed and developed as previously described. All compounds in Examples 9 to 17 insolubilised the resin to some degree. With the exception of Examples 17 and 12, which were only slightly solubilised, all the Examples gave a reasonable differential between exposed and non-exposed areas with respect to the rate of dissolution of the coating in dilute sodium metasilicate pentahydrate. Compound Nos. 9, 11, 15 and 16 were found to be somewhat better than those of Examples 10 and 13. It was also observed that the addition of diphenyliodonium-2-carboxylate gave only a very poorly, if at all insolubilised phenolic resin. This is probably because the betaine structure having intramolecular charge compensation inhibits intermolecular association with the resin.

Examples 18 to 22

The following Examples demonstrate the behaviour of a novolac type resin with the addition of an iodonium salt and various levels of amine.

5 g of CRJ 406 phenolic resin was dissolved in 15 g methanol. To this was added 0.8 g of diphenyliodonium hexafluorophosphate (~16% by weight of resin). The amounts of tri-n-butylamine then added to 2.5 g aliquots of the resin/iodonium solution are given in Table 4.

Table 4

Example No.	Amount of Bu ₃ N (g)	Molar ratio of iodonium:amine
18	0	-
19	0.025	1:0.58
20	0.050	1:1.16
21	0.075	1:1.74
22	0.1	1:2.3

Coatings were made using these solutions by the procedures described earlier and the samples were then exposed, and subsequently developed, in dilute sodium metasilicate pentahydrate solution. It had been observed on previous occasions, and again in this series of experiments, that the addition of base to the iodonium/resin system increases or at least accelerates the interaction between the two compounds. This is not unexpected as the phenolic resin, which is the electron donor, is converted to the anionic form, which will associate more readily with the iodonium salt, i.e. the electron acceptor.

The physical effect of this is seen by the increase in alkali resistance exhibited by coatings to which a small amount of base has been added. For example, in Example 18 no amine was added and the alkali resistance of the coating was about 75 seconds. In Example 19, which had a small amount of amine added, the alkali resistance dramatically rose to in excess of 10 minutes. It is desirable to have a coating as resistant to alkali as possible to begin with so there is the scope to obtain a large differential in solubility after exposure. The result of the exposures and development of Examples 18 to 22 are shown in Table 5.

Table 5

Example No.	Colour in irradiated areas	Development time to clear background
18	red	-*
19	pink	15 mins
20	slightly yellow	1 min
21	slightly mauve	30 secs
22	mauve	15 secs

* Only a poor differential.

There are a number of trends which can be seen from Tables 4 and 5. Example 18 shows that although quite an intense red image forms in irradiated areas, the coating did not markedly photosolubilise in comparison to the other Examples. The mechanisms which occur are not fully understood but it is very likely that, as iodonium salts are oxidising agents and phenols can be oxidised to red products, the red image is caused by an oxidation product of the phenolic resin. As the phenolic resin relies on the -OH groups for its alkali solubility, then oxidation of these to keto groups will reduce or prevent dissolution in base.

The addition of amine appeared to prevent this reaction occurring and it can be seen that, quite dramatically as increasing amounts of amine are added, the red colour in exposed areas becomes fainter, eventually disappearing altogether to leave a yellowish image. Upon further addition of amine, a mauve colouration appears. At the same time, the system becomes more and more photosolubilising with the major difference being seen between Examples 19 and 20. These two Examples correspond to amine:iodonium ratios of 0.58:1 to 1.16:1. As discussed earlier, there is a 1:1 reaction ratio between amine and iodonium in this system and if a large excess of amine is added it can be deleterious to the storage properties of the system, due to "dark" reactions between iodonium salts and amines.

Examples 23 to 26

The following four Examples demonstrate systems incorporating a source of hydrogen ions which give very good visible images in exposed areas due to dye formation.

2.5 g of CRJ 406 resin was dissolved in 11.5 g of butan-2-one and to this was added 0.7 g of diphenyliodonium hexafluorophosphate. Various amounts of bis(4-dimethylaminophenyl)methane (BDAPM) were then added to 3.675 g aliquots as shown in Table 6.

Table 6

Example No.	Amount of Amine (g)	Molar ratio of iodonium:amine
23	0	-
24	0.14	1:1.34
25	0.175	1:1.68
26	0.2	1:1.92

Coatings were made using these solutions and a K-2 wire-wound coating bar onto an aluminium substrate. The coatings were dried at 85°C for 90 seconds before evaluation.

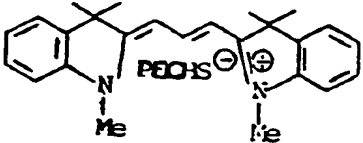
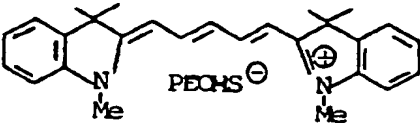
Exposures were made using the PL 5000 exposing frame at a distance of 0.7 m for 16 units, with subsequent development in 6% aqueous sodium metasilicate pentahydrate. The results of this series of experiments show that Example 23 had not photosolubilised very efficiently and also did not have a blue image in exposed areas, whereas Examples 24 to 26 all had very deep blue images which dissolved easily in the developer. There was no significant difference between them. The unexposed regions of all samples withstood longer than 10 minutes immersion in developer without significantly dissolving, thus giving a high contrast in solubility between exposed and non-exposed areas. The BDAPM contributes to this solubility differential as described earlier.

The following Examples 27 to 29 demonstrate the ability of the phenolic resin/iodonium system to be sensitised to visible light.

Examples 27 and 28

A stock solution containing 25% w/w Aroclene 24780 in butan-2-one was prepared. To a 5 g aliquot of this solution were added 0.2 g of diphenyliodonium hexafluorophosphate and 0.02 g of a cyanine dye shown in Table 7.

Table 7

Example No.	Dye	λ_{\max}
27		555 nm
28		645 nm

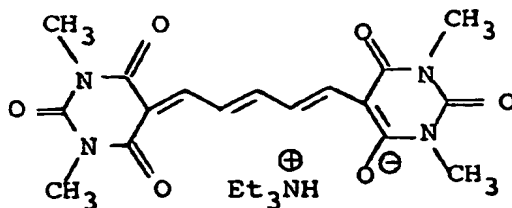
PECHS = perfluoro(4-ethylcyclohexyl)sulphonate

Coatings were prepared using a K-3 wire-wound coating bar onto an aluminium substrate. Samples were air dried for three days before use. Exposures of these two coatings were carried out in two different ways.

In one instance a 150 Watt xenon lamp was used as the source. This was positioned 7.6 cm (3") away from the sample, over which was placed a No. 4 Kodak Wratten filter. This only permits light of wavelengths - 460 nm to be transmitted, so that only light corresponding to the absorption of the cyanine dyes is absorbed. The samples were exposed for 10 minutes, after which they were immersed in an aqueous sodium metasilicate pentahydrate solution. Both samples preferentially dissolved in the exposed regions, demonstrating that photosolubilisation had occurred.

Example 29

To 5 g of a 25% w/w BKR 2620 resin in butan-2-one were added 0.2 g of diphenyliodonium hexafluorophosphate and 0.04 g of the oxonol dye shown below:



λ_{\max} 590 nm

A coating on aluminium was prepared as in the previous two Examples. In this case the coating was dried at 50°C for 30 minutes before use.

The exposure source in this case was a 1 mW He-Ne laser which emits at 630 nm. The spot size was 1.3 mm diameter and exposure time was 10 seconds; this corresponds to $\sim 10^6$ mJ/m².

Subsequent development in a 3% aqueous sodium metasilicate pentahydrate solution preferentially dissolved the irradiated areas. This experiment shows that although the λ_{\max} of the dye was ~ 40 nm from the emission of the laser, sufficient energy was absorbed to achieve photosolubilisation.

The following Examples 30 to 34 show how the phenolic resin/iodonium system can be sensitised to the output of an Argon ion laser emitting at 488 nm.

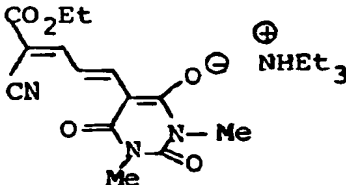
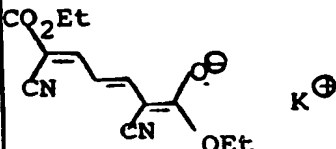
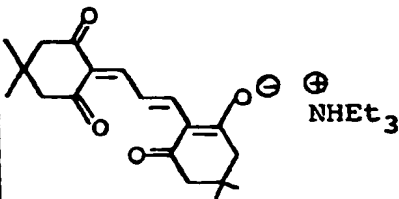
Examples 30 to 32

1.25 g of a 25% Aroclene 24780 resin solution in butan-2-one was mixed with 0.1 g diphenyliodonium hexafluorophosphate and 0.02 g of the oxonol type dyes shown in Table 8.

The coatings were made with a K-2 wire-wound bar onto an aluminium substrate and were dried for two minutes at 85°C.

The samples were exposed to the output of a nominally 10 mW Argon Ion laser, through a 1.91 neutral density filter. Dwell times were varied for 5 ms, 1.8 ms, 0.5 ms, 180 μ s, 50 μ s, to 18 μ s. The samples were then developed in 6% aqueous sodium metasilicate pentahydrate for 1 to 1.5 minutes. Microscopic study of the resultant samples indicate that the 18 μ s dwell time was sufficient exposure for solubilisation to occur. Calibration of the laser energy at the sample surface for an 18 μ s dwell time suggests a sensitivity of 1.025×10^5 mJ/m².

Table 8

Example	Dye	λ_{\max}
30		460 nm $E = 6.5 \times 10^4$
31		450 nm $E = 1.0 \times 10^5$
32		502 nm $E = 1.2 \times 10^5$

Example 33

A similar experiment was run using CRJ 406 resin; a coating was made from a solution of 1.25 g of a 25% CRJ 406 resin in butan-2-one with 0.05 g of diphenyliodonium hexafluorophosphate and 0.02 g of oxonol dye shown in Example 31 in Table 8.

Exposures were made as previously described. After development in 6% aqueous sodium metasilicate pentahydrate, examination under an optical microscope revealed that the 50 μ s dwell time was sufficient exposure to solubilise the coating

Example 34

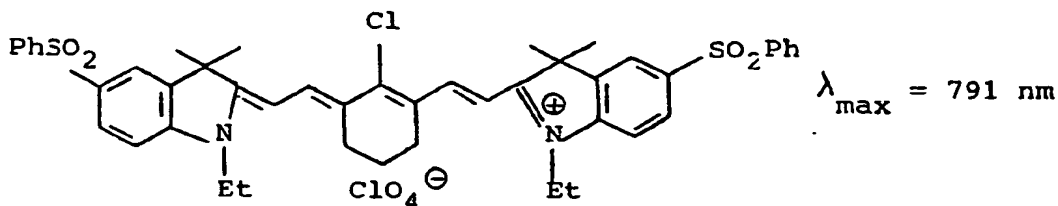
A coating was prepared from a solution containing 1.25 g of 25% CRJ 406 resin in butan-2-one with 0.05 g of diphenyliodonium hexafluorophosphate, 0.05 g of bis(p-dimethylaminophenyl)methane, and 0.02 g of the oxonol dye shown in Example 30 (Table 8).

Exposures were made as previously described and after development in 6% sodium metasilicate pentahydrate, examination under an optical microscope revealed that a 50 μ s exposure was sufficient to cause solubilisation of the coating.

The following Examples 35 to 38 show how the phenolic resin/iodonium system can be sensitised to infrared irradiation by the use of cyanine dyes.

Example 35

1.25 g of a 25% Arofene 24780 resin solution in butan-2-one was mixed with 0.06 g of diphenyliodonium hexafluorophosphate and 0.005 g of the heptamethinecyanine dye shown below:



A coating on aluminium was prepared using a No. 3 wire-wound bar in the normal way; the sample was air dried before evaluation. The exposure source was a laser diode emitting at 812 nm, with a power output of $\sim 10^6$ mJ/m². The laser was fitted with scanning capabilities, thus enabling the exposure to be varied by varying the dwell times of the laser spot on the sample. Exposures were made where dwell times were used of 5 ms, 500 μ s, 50 μ s and 5 μ s. Subsequent development of the sample using 6% sodium metasilicate pentahydrate cleared the 50 μ s spots and the 5 μ s spots could be seen. The former value corresponds to a sensitivity of approximate 10^6 mJ/m².

Examples 36 to 38

These Examples are as in Example 35 but using a somewhat higher level of dye and extending the range of the dyes by varying the N-alkyl group. The coatings were made from the following formulation: 1.25 g of a 25% w/w Arofene 24780 resin solution in butan-2-one with 0.06 g of diphenyliodonium hexafluorophosphate and 0.02 g of a cyanine dye shown in Table 9.

Table 9

Example No.	Dye	R	λ_{\max}
36		ethyl	791 nm
37		n-butyl	794 nm
38		n-hexyl	792 nm

Samples of each of these coatings were exposed using the laser diode as described in Example 35.

Subsequent development in 6% sodium metasilicate pentahydrate preferentially dissolved the 50 μ s spots. This corresponds to a sensitivity of approximately 5×10^5 mJ/m².

Example 39

0.1 g of diphenyliodonium hexafluorophosphate was dissolved in 5 g of a 25% w/w solution of BKR 2620 in butan-2-one. Coatings were made with this solution as previously described and, after air drying, they were further dried at 100°C for a few minutes. Images were made using standard Fogra PMS2 and Ugra/Gretag targets in a Parker Graphics PL 5000 flip-top exposing frame equipped with a 5 kW metal halide source. Exposure time was 40 seconds which corresponds to the exposure needed for positive-acting printing plates which are currently on the market. After exposure, development was achieved by immersion in 6% aqueous sodium metasilicate pentahydrate for 80 seconds with gentle agitation.

The resultant plate was run on a Multilith offset press for a short number of prints (ca. 100). The plate inked rapidly upon roll-up and no problems were noticed during the test run. The sample held 2 to 99% dots on a 60 lines per cm screened target, 8 to 96% dots on a 120 lines per cm screened target and resolved a 6 μ m line.

Example 40

This Example demonstrates that printing plates prepared from an iodonium/phenolic resin system can run for many thousands of copies without breakdown on press.

A solution was prepared containing 8.0 g of 25% w/w of Reichhold 29802 resin in butan-2-one; 0.1 g of diphenyliodonium hexafluorophosphate and 0.1 g of the yellow oxonol dye shown in Example 31. To 2.5 g of this solution 0.02 g of cellulose acetate butyrate was added and a coating was prepared on a grained aluminium substrate using a No. 6 Meyer, wire-wound coating bar. The coating was dried for 2 minutes at 85°C. The printing plate was then exposed on an Ascor exposure unit for about 15 seconds using standard test targets and grey scales. Subsequent development using 5.8% sodium metasilicate pentahydrate developer removed the irradiated areas giving a high quality image of hydrophobic resin on an aluminium substrate. This plate was then run on press which was set up in an accelerated wearing mode. By comparing the run length of the experimental plate to commercial plates of known run length it was shown that the experimental plate ran for at least as long as the standard plates. This corresponds to approximately 200,000 copies on a normally prepared press.

Example 41

This Example demonstrates the use of sulphonium salts in the present invention.

5 g of a 25% w/w solution BKR 2620 resin in butan-2-one was added 0.2 g of triphenylsulphonium hexafluorophosphate. This solution was used to prepare a coating on a slurry-grained aluminium substrate using a K-3 wire-wound coating bar. Before evaluation the coating was dried at 100°C for one minute. Exposures of the sample was carried out using a 5 kW metal halide lamp at a distance of 0.7 m for about

30 seconds.

Development of the sample was achieved by immersion in a 6% aqueous sodium metasilicate pentahydrate for 100 seconds with slight agitation thus removing the exposed areas. Using this procedure samples can be produced with 3 to 97% dot retention on a 60 lines per cm screen target.

Example 42

This Example demonstrates the feasibility of the resin-iodonium system to be useful as a colour proofing "tripack". The addition of an inert colourant is required to give the resultant image.

Three solutions were prepared containing 5 g of 25% w/w solution BKR 2620 resin in butan-2-one and 0.2 g diphenyliodonium hexafluorophosphate. To separate solutions were added 0.35 g of Waxoline Yellow TS, 0.025 g Victoria Blue and 0.1 g Waxoline Rubin. Coatings were prepared from these solutions using a No. 3 K-bar and 0.1 mm (0.004 in) clear polyester film as the substrate. After drying, the coatings were imaged in a vacuum frame using the appropriate colour separation target.

Exposure time was one minute and subsequent development was achieved by immersion in 3% w/w sodium metasilicate pentahydrate solution. The full colour original could be reconstructed by aligning the three sheets one upon each other to give a "tripack".

Example 43

This Example demonstrates how an overhead projector can be used as a light source to produce enlarged copies from an original. These may have use as temporary signs, etc.

A coating solution was prepared containing 2.5 g of 25% w/w solution CRJ 406 resin, 0.1 g diphenyliodonium hexafluorophosphate and 0.084 g of the yellow dye of Example 31.

A coating was prepared from this solution using a K-3 wire-wound bar and an aluminium substrate. After drying for 2 minutes at 85°C exposures were made by fastening a 15 x 15 cm sample onto a vertical surface and then projecting an image into this using a Model 229SL overhead projector positioned so as to give a tenfold enlargement in area. The exposure took 300 seconds and was carried out in a darkened room. Subsequent development in 3% sodium metasilicate pentahydrate solution preferentially dissolved the irradiated areas, leaving an enlarged copy of the original.

Example 44

0.175 g of diphenyliodonium hexafluorophosphate and 0.14 g of bis-p-dimethylaminophenylmethane was added to 2.5 g of a 25% w/w solution of CRJ 406 resin in butan-2-one. Coatings were then prepared using a K-2 wire-wound coating bar onto an aluminium substrate. The coated substrate was then dried at 85°C for 3 minutes in the dark.

To demonstrate the normal photosolubilising behaviour of this formulation an imaging exposure was made using a Parker Graphic PL 5000 exposure source for 25 units at a distance of 0.7 m. Subsequent development in 5.6% w/w aqueous sodium metasilicate pentahydrate preferentially dissolved the exposed areas giving a good quality, positive-acting printing plates.

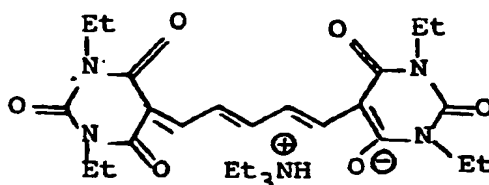
Two samples of this coating were exposed through standard test targets for 25 units at 0.7 m. These samples were then heated for 30 seconds and 60 seconds at 120°C respectively. Each coating was then given a second overall exposure to ultraviolet radiation (25 units at 0.7 m) followed by development in 5.6% w/w aqueous sodium metasilicate pentahydrate. The results showed that the samples which had been subjected to 120°C for 30 seconds and 60 seconds both gave overall negative-acting coatings.

Example 45

The formulation used was identical to that used in Example 44 except that the CRJ 406 resin was replaced with BKR 2620 resin. The results were also identical in that sample heated to 120°C for 30 seconds and 60 seconds gave overall negative-acting plates.

Example 46

0.09 g of diphenyliodonium hexafluorophosphate, 0.02 g of the yellow oxonol dye used in Example 43 and 0.002 g of a blue oxonol dye of the formula:



10 were added to 1.25 g of a 25% w/w CRJ 406 resin solution in butan-2-one. The solution was coated onto an aluminium substrate using a K-2 wire-wound bar and dried at 85°C for 3 minutes.

The coated plate exhibited the normal photosolubilising mode on exposure to test targets for 13 units at 0.7 m, followed by development in aqueous sodium metasilicate pentahydrate, whereupon the exposed portions preferentially dissolved leaving a high quality, positive-acting printing plate.

15 Three samples from the same coatings were also imaged for 13 units followed by heating at 120°C for 30, 60 and 90 seconds, respectively, followed by an overall ultraviolet exposure for 13 units, then development in 5.6% w/w aqueous sodium metasilicate pentahydrate. The results were that overall negative-acting systems were obtained.

20 Example 47

0.02 g of the yellow oxonol dye used in Example 43, 0.002 g of the blue oxonol dye used in Example 46 and 0.02 g of diphenyliodonium hexafluorophosphate were added to 2.5 g of a 25% w/w BKR 2620 resin solution in butan-2-one. Coatings were made using a K-2 wire-wound bar onto an aluminium substrate and
25 dried at 85°C for 3 minutes.

To demonstrate the normal positive action of the coated plate, a sample was exposed for 15 units at 0.7 m followed by development in dilute aqueous sodium metasilicate pentahydrate to give a positive image. If the sample was given an additional drying time for 30 seconds to 4 minutes at 120°C before normal drying exposure, a positive system was still obtained although the rate of photosolubilisation was much slower.
30 This is thought to be because the additional heating at 120°C markedly increases the alkali resistance of the coating.

A second series of samples were also subjected to an additional drying time for 30 seconds to 4 minutes at 120°C before being imaged through standard test targets for 15 units. After imaging they were heated at 120°C for 60 seconds and then subjected to an overall ultra-violet exposure (15 units at 0.7 m).
35 Subsequent development in aqueous sodium metasilicate pentahydrate preferentially dissolved away the non-imaged areas leaving an overall negative sample. The quality of these samples varied depending on the additional drying time, with the optimum being in the region of an additional 60 seconds at 120°C.

Example 48

0.175 g of diphenyliodonium hexafluorophosphate was added to 2.5 g of a 25% w/w CJR 406 resin solution in butan-2-one. Coatings were prepared from this solution by using a K-2 wire-wound coating bar onto an aluminium substrate. The coating was dried for 3 minutes at 85°C. A sample was exposed for 25 units at 0.7 m followed by an overall heating at 120°C for 60 seconds, then an overall ultraviolet exposure
45 for 25 units at 0.7 m. Development in aqueous sodium metasilicate pentahydrate preferentially washed out the non-imaged areas giving an overall negative-acting system, although the differential in solubility between imaged and non-imaged areas was not large.

Examples 49 and 50

50 Compositions containing phosphonium salts

10 g of BKR 2620 resin was dissolved in 30 g of butan-2-one.

To 2.5 g aliquots of the resin solution was added:

56 Example 49: 0.1 g of benzyltriphenylphosphonium hexafluorophosphate.

Exempl 50: 0.1 g of benzyltriphenylphosphonium hexafluorophosphate and 0.1 g of bis(4-dim thylaminophenyl)methane.

Using these solutions, coatings were made on an aluminium substrate using a No. 2 wire-wound coating

bar. The coatings were then dried at 85°C for 6 minutes. Exposures were made using a NuArc flip-top platemaker for 500 units.

Subsequent development in 6% aqueous sodium metasilicate pentahydrate preferentially dissolved the exposed areas of the coatings.

5 Example 51

Example 49 was repeated using 2.5 g of a 25% CRJ 406 resin in place of the BKR 2620 resin. After 500 units of exposure, the irradiated areas were preferentially dissolved in 6% aqueous sodium metasilicate pentahydrate developer.

Examples 52 and 53

Compositions containing sulfoxonium salts.

15 A 25% w/w solution of BKR 2620 resin in butan-2-one was prepared.

To 2.5 g aliquots of the resin solution was added:

Example 52: 0.1 g of triphenylsulfoxonium hexafluorophosphate.

Example 53: 0.1 g of triphenylsulfoxonium hexafluorophosphate and 0.1 g of bis(4-dimethylaminophenyl)methane.

20 Using these solutions, coatings were prepared using a No. 2 wire-wound coating bar on an aluminium substrate. The coatings were dried for 6 minutes at 85°C. Exposures were then made using the NuArc flip-top platemaker for 100 units. Subsequent development in 3% aqueous sodium metasilicate pentahydrate preferentially dissolved the exposed areas.

25 Example 54

Compositions containing aryloxysulphonium salts.

30 To 3.0 g of a 25% w/w solution of BKR 2620 resin in butan-2-one was added 0.25 g of diphenyl methoxysulphonium tetrafluoroborate. Using this solution a coating was made onto an aluminium substrate using a No. 3 wire-wound coating bar. The coating was then dried for 6 minutes at 85°C. The sample was exposed for 100 units on a NuArc flip-top platemaker and then developed in 6% aqueous sodium metasilicate pentahydrate solution. The exposed areas preferentially dissolved showing that photosolubilisation had occurred.

Example 55

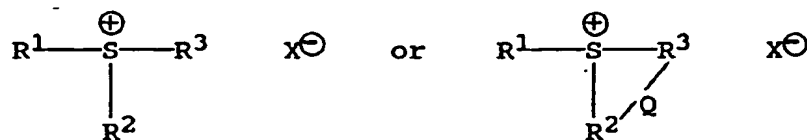
40 To 2.5 g of 25% w/w solution of CRJ 406 resin in butan-2-one, 0.1 g of diphenylmethoxysulphonium hexafluorophosphate was added. Using this solution a coating was made onto an aluminium substrate using a No. 3 wire-wound coating bar. The coating was dried for 6 minutes at 85°C. The sample was then exposed for 100 units using a NuArc flip-top platemaker. After exposure the sample was developed in 3% aqueous sodium metasilicate pentahydrate solution whereupon the exposed areas preferentially dissolved.

45 Example 56

To 5.0 g of a 25% w/w solution of CRJ 406 resin in butan-2-one was added 0.1 g of diphenyliodonium hexafluorophosphate, 0.04 g of the oxonol dye used in Example 31 and 0.18 g of bis(4-dimethylaminophenyl) methane. This solution was then coated onto an aluminium substrate using a No. 2 wire-wound coating bar and dried for 3 minutes at 85°C. Exposures were then made using a NuArc flip-top platemaker and the samples were subsequently developed in a 3% aqueous solution of sodium metasilicate pentahydrate. This coating, which had a visible image after exposure, required only 10 units (approximately 8 seconds) exposure to achieve complete solubilisation within 20 seconds in the developer. The unexposed areas were highly resistant to developer: only approximately 10% of the coating weight was lost after immersion for 180 seconds in an aqueous solution of 3% sodium metasilicate pentahydrate.

Claims

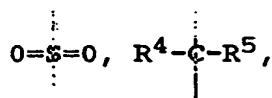
1. A radiation-sensitive composition comprising an alkali-soluble phenolic resin and a radiation-sensitive onium salt characterised in that the composition is photosolubilisable, and the onium salt has one of the following formulae:



in which:

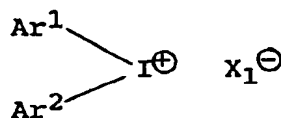
at least one of R¹, R² and R³ is an optionally substituted aromatic group,

Q is a carbon-to-carbon bond or a linking group selected from O, S, >S=O, >C=O,



or >N-R⁵, in which R⁴ and R⁵ are independently selected from H, an alkyl group having from 1 to 4 carbon atoms, and an alkenyl group having from 2 to 4 carbon atoms and R⁵ is an aryl group having from 6 to 20 carbon atoms or an acyl group having from 2 to 20 carbon atoms; and

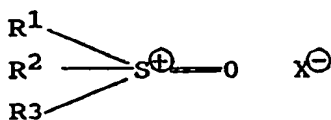
X[⊖] is an anion,



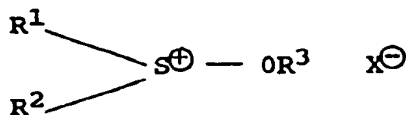
in which:

Ar¹ and Ar² independently represent aromatic groups which are optionally substituted and optionally linked together to include the iodine atom within a ring structure; and,

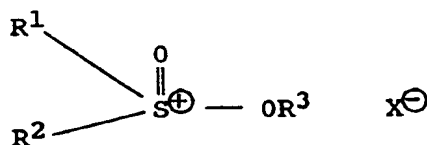
X₁[⊖] represents an inorganic anion, or an organic anion of the formula R⁸COO[⊖] or R⁸SO₃[⊖] in which R⁸ represents an alkyl or aryl group;



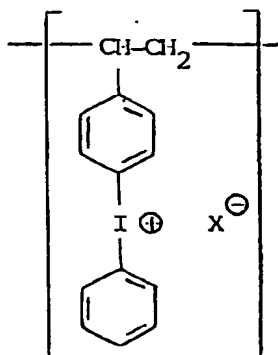
in which R¹ to R³ are as defined above, with the exception that each of R¹ to R³ may represent optionally substituted aliphatic groups,



in which R¹ to R³ are as defined above, with the exception that each of R¹ to R³ may represent optionally substituted aliphatic groups,

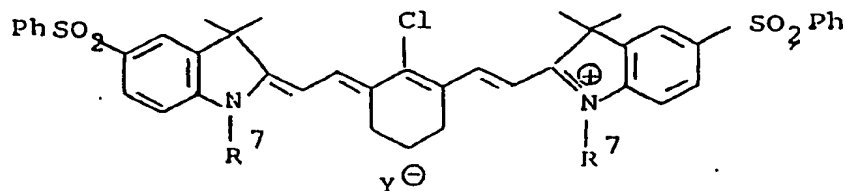


in which R^1 to R^3 are as defined above, with the exception that each of R^1 to R^3 may represent optionally substituted aliphatic groups, and a polymer including the monomeric units of the formula:

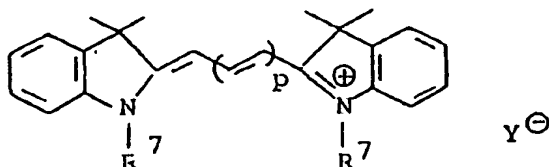


in which X^{\ominus} is an anion.

2. A composition as claimed in Claim 1 characterised in that the resin is a novolac resin and the onium salt is present in an amount from 1 to 40% by weight of the total weight of phenolic resin and onium salt.
3. A composition as claimed in Claim 1 characterised in that the resin is a resole resin and the onium salt is present in an amount from 5 to 40% by weight of the total weight of phenolic resin and onium salt.
4. A composition as claimed in any preceding Claim characterised in that the anion is selected from halide, $\text{H}_2\text{SO}_4^{\ominus}$, $\text{R}^8\text{CO}_2^{\ominus}$, in which R^8 represents an optionally substituted alkyl or phenyl group, and a halogen-containing complex ion.
5. A composition as claimed in any preceding claim additionally comprising a spectral sensitiser in an amount up to 10% by weight of the total weight of phenolic resin, onium salt and spectral sensitiser.
6. A composition as claimed in Claim 5 characterised in that the spectral sensitiser is selected from one of the following classes: diphenylmethane, xanthene, acridine, methine and polymethine (including oxonol, cyanine and merocyanine) dye, thiazole, thiazine, azine, aminoketone, porphyrin, coloured aromatic polycyclic hydrocarbon, p-substituted aminostyryl compound, aminotriazolyl methane, polyarylene, polyarylpolyyene, 2,5-diphenylisobenzofurane, 2,5-diarylcyclopentadiene, diarylfuran, diarylthiofuran, diarylpyrrole, polyarylphenylene, coumarin and polyaryl-2-pyrazoline.
7. A composition as claimed in Claims 6 or 7 characterised in that the spectral sensitiser has the formula:



or



In which:

R⁷ represents an alkyl group of 1 to 6 carbon atoms,Y^o represents 4-perfluoroethylcyclohexylsulphonate or ClO₄^o, and,

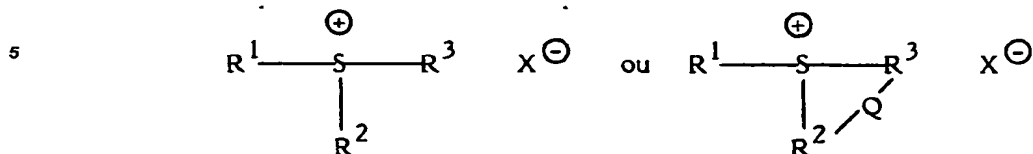
p is 1 or 2.

8. A composition as claimed in any preceding claim additionally comprising an amine in an amount up to 25% by weight of the total weight of phenolic resin, onium salt and amine.
9. A composition as claimed in Claim 8 characterised in that the molar ratio of amine to onium salt is approximately 1 : 1.
10. A composition as claimed in Claim 8 or Claim 9 characterised in that the amine is tri-n-butylamine or bis(4-dimethylaminophenyl)methane.
11. A radiation-sensitive element comprising a layer of the composition of any one of the preceding claims coated on a substrate.
12. An element as claimed in Claim 11 characterised in that the substrate is paper, aluminium, copper, copper-epoxy laminated board, polyester film or silica.
13. A method of producing a lithographic image on an element as claimed in Claim 11 or Claim 12 comprising:
 - image-wise exposing said element to actinic radiation, and,
 - developing the plate with an alkali-based developer so that the composition is removed in the irradiated areas thereby producing said image.
14. A method of producing a lithographic image on an element as claimed in Claim 11 or Claim 12 comprising:
 - image-wise exposing said element to actinic radiation,
 - heating the element so as to convert the coating in the irradiated areas to a form insoluble to alkali,
 - further exposing the element overall to actinic radiation so that areas not previously exposed are rendered alkali-soluble, and,
 - developing the element with an alkali-based developer so that the coating is removed from those areas of the element rendered soluble by said further exposure thereby producing said image.
15. A method as claimed in Claim 13 or 14 characterised in that the developer is aqueous sodium metasilicate.

Revendications

1. Composition sensible au rayonnement comprenant une résine phénolique soluble dans les alcalis et un

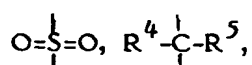
sel d'onium sensible au rayonnement, caractérisée en ce qu'elle est photosolubilisable et en ce que le sel d'onium répond à une des formules suivantes :



dans lesquelles :

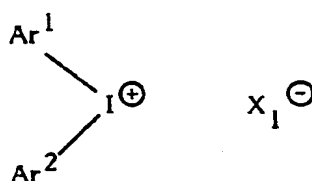
au moins l'un des R^1 , R^2 et R^3 est un groupe aromatique éventuellement substitué,

Q est une liaison carbone-carbone ou un groupe de liaison choisi parmi O, S, $>\text{S}=\text{O}$, $>\text{C}=\text{O}$,



ou $>\text{N}-\text{R}^6$, où R^4 et R^5 sont choisis indépendamment parmi H, un groupe alkyle de 1 à 4 atomes de carbone et un groupe alcényle de 2 à 4 atomes de carbone, et R^6 est un groupe aryle comportant 6 à 20 atomes de carbone ou un groupe acyle de 2 à 20 atomes de carbone ; et

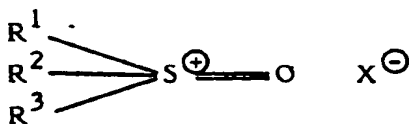
X^\ominus est un anion,



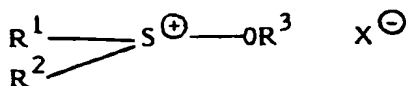
dans la formule duquel :

Ar^1 et Ar^2 représentent indépendamment des groupes aromatiques qui sont facultativement substitués et facultativement liés ensemble pour inclure l'atome d'iode dans une structure cyclique ; et

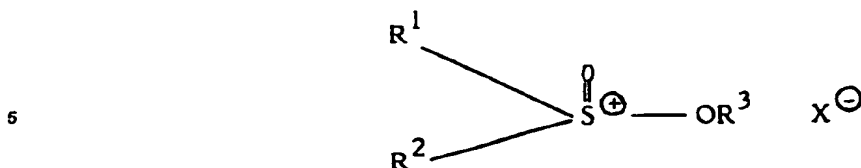
X_1^\ominus représente un anion inorganique ou un anion organique de la formule $\text{R}^8\text{COO}^\ominus$ ou $\text{R}^8\text{SO}_3^\ominus$ où R^8 représente un groupe alkyle ou aryle ;



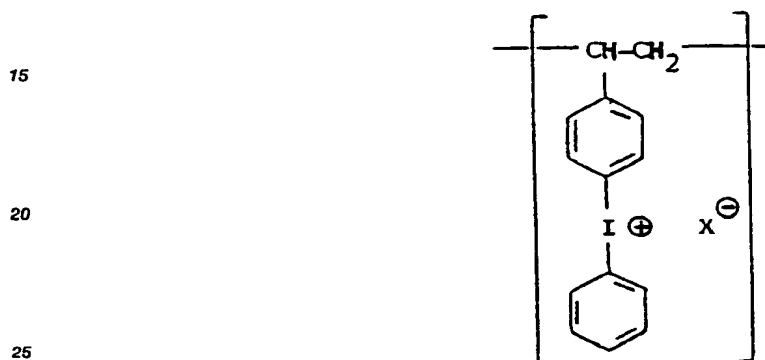
où R^1 à R^3 ont la définition précédente, sauf que chacun des R^1 à R^3 peut représenter des groupes aliphatiques éventuellement substitués ;



où R^1 à R^3 ont la définition donnée précédemment, sauf que chacun des R^1 à R^3 peut représenter des groupes aliphatiques éventuellement substitués ;

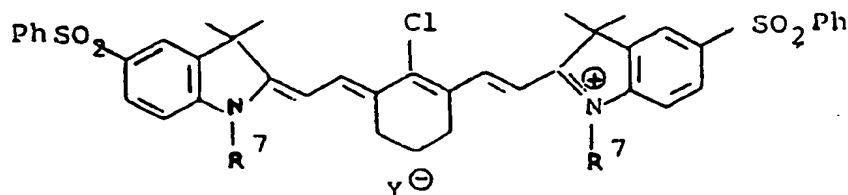


10 où R^1 à R^3 ont la définition donnée précédemment, sauf que chacun des R^1 à R^3 peut représenter des groupes aliphatiques éventuellement substitués, et un polymère comprenant des unités monomères de la formule :

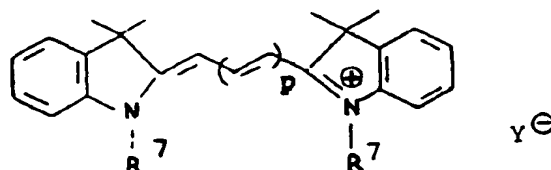


dans laquelle X^{\ominus} est un anion.

- 30 2. Composition suivant la revendication 1, caractérisée en ce que la résine est une résine novolaque et en ce que le sel d'onium se trouve en une quantité de 1 à 40 % en poids du poids total de la résine phénolique et du sel d'onium.
- 35 3. Composition suivant la revendication 1, caractérisée en ce que la résine est une résine de résole, et en ce que le sel d'onium se trouve en une quantité de 5 à 40 % en poids du poids total de la résine phénolique et du sel d'onium.
- 40 4. Composition suivant l'une quelconque des revendications précédentes, caractérisée en ce que l'anion est choisi parmi les halogénures, $\text{H}_2\text{SO}_4^{\ominus}$, $\text{R}^8\text{CO}_2^{\ominus}$, où R^8 représente un groupe alkyle ou phényle éventuellement substitué, et un ion complexe contenant un halogène.
- 45 5. Composition suivant l'une quelconque des revendications précédentes, comprenant en outre un agent de sensibilisation spectrale en une quantité allant jusqu'à 10 % en poids du poids total de la résine phénolique, du sel d'onium et de l'agent de sensibilisation spectrale.
- 50 6. Composition suivant la revendication 5, caractérisée en ce que l'agent de sensibilisation spectrale est choisi parmi l'une des classes suivantes : colorants de diphenylméthane, xanthène, acridine, méthine et polyméthine (notamment oxonol, cyanine et mérocyanine), thiazole, thiazine, azine, aminocétone, porphyrine, hydrocarbure polycyclique aromatique coloré, composé aminostyryle p-substitué, aminotriazolyl méthane, polyarylène, polyarylpolyène, 2,5-diphénylisobenzofuranne, 2,5-diarylcyclopentadiène, diarylfuranne, diarylthiofuranne, diarylpyrrole, polyarylphénylène, coumarine et polyaryl-2-pyrazoline.
- 55 7. Composition suivant la revendication 5 ou 6, caractérisée en ce que l'agent de sensibilisation spectrale répond aux formules :



ou



dans lesquelles :

R⁷ représente un groupe alkyle de 1 à 6 atomes de carbone,Y^o représente du 4-perfluoréthylcyclohexylsulfonate ou ClO₄^o, et

p est égal à 1 ou 2.

8. Composition suivant l'une quelconque des revendications précédentes, comprenant en outre une amine en une quantité allant jusqu'à 25 % en poids du poids total de la résine phénolique, du sel d'onium et de l'amine.
9. Composition suivant la revendication 8, caractérisée en ce que le rapport molaire de l'amine au sel d'onium est d'environ 1/1.
10. Composition suivant la revendication 8 ou la revendication 9, caractérisée en ce que l'amine est de la tri-n-butylamine ou du bis-(4-diméthylaminophényl)méthane.
11. Élément sensible au rayonnement, comprenant une couche de la composition suivant l'une quelconque des revendications précédentes, appliquée sur un substrat.
12. Élément suivant la revendication 11, caractérisé en ce que le substrat est formé de papier, aluminium, cuir, plaque stratifiée de cuivre-résine époxy, film de polyester ou silice.
13. Procédé de production d'une image lithographique sur un élément tel que revendiqué dans la revendication 11 ou la revendication 12, caractérisé en ce qu'il comprend :
l'exposition de l'élément susdit selon une image à un rayonnement actinique, et
le développement de la plaque avec un révélateur à base d'alcali de manière que la composition soit enlevée dans les zones irradiées en produisant de la sorte l'image susdite.
14. Procédé de production d'une image lithographique sur un élément tel que revendiqué dans la revendication 11 ou la revendication 12, caractérisé en ce qu'il comprend :
l'exposition de l'élément susdit selon une image à un rayonnement actinique,
le chauffage de l'élément de manière à convertir la couche dans les zones irradiées à une forme insoluble dans les alcalis,
une nouvelle exposition de l'élément dans son ensemble à un rayonnement actinique de manière que les zones qui n'ont pas été exposées précédemment soient rendues solubles dans les alcalis, et
le développement de l'élément avec un révélateur à base d'alcali de manière que la couche soit enlevée depuis les zones de l'élément rendues solubles par la nouvelle exposition susdite, en produisant de la sorte l'image précitée.
15. Procédé suivant la revendication 13 ou la revendication 14, caractérisé en ce que le révélateur est constitué par une solution aqueuse de métasilicate de sodium.

Patentansprüche

1. Strahlungsempfindliche Zusammensetzung, umfassend ein Alkali-lösliches phenolisches Harz und ein strahlungsempfindliches Oniumsalz, dadurch gekennzeichnet, daß die Zusammensetzung durch Licht lösbar zu machen ist und das Oniumsalz eine der folgenden Formeln aufweist:

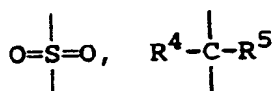


in denen:

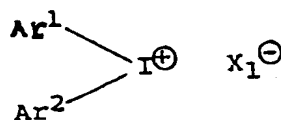
mindestens einer der Reste R^1 , R^2 und R^3

ein gegebenenfalls substituierter aromatischer Rest ist,

Q eine Kohlenstoff-Kohlenstoff-Bindung oder eine Verbindungsgruppe, ausgewählt aus O, S, $>\text{S}=\text{O}$, $>\text{C}=\text{O}$,

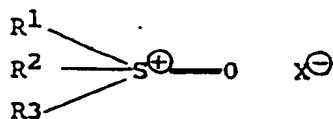


oder $>\text{N}-\text{R}^6$ ist, wobei R^4 und R^5 unabhängig aus H, einem 1 bis 4 Kohlenstoffatome aufweisenden Alkylrest und einem 2 bis 4 Kohlenstoffatome aufweisenden Alkenylrest ausgewählt sind und R^6 ein 6 bis 20 Kohlenstoffatome aufweisender Arylrest oder ein 2 bis 20 Kohlenstoffatome aufweisender Acylrest ist und X^{\ominus} ein Anion ist,

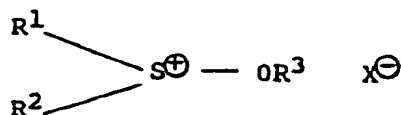


In der:

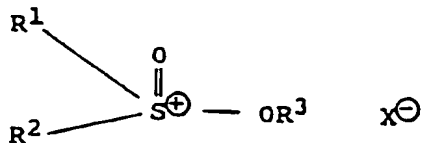
Ar^1 und Ar^2 unabhängig aromatische Reste darstellen, die gegebenenfalls substituiert und gegebenenfalls zum Einschluß des Jodatoms in eine Ringstruktur miteinander verbunden sind, und X_1^{\ominus} ein anorganisches Anion oder ein organisches Anion der Formel $\text{R}^8\text{COO}^{\ominus}$ oder $\text{R}^8\text{SO}_3^{\ominus}$ darstellt, in der R^8 einen Alkyl- oder Arylrest darstellt;



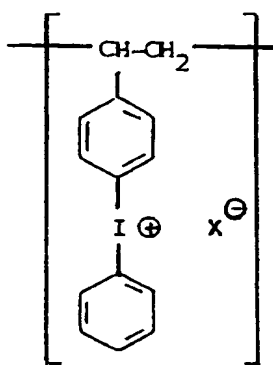
in der R^1 bis R^3 wie oben definiert sind, mit der Ausnahme, daß alle Reste R^1 bis R^3 gegebenenfalls substituierte aliphatische Reste darstellen können,



in der R^1 bis R^3 wie oben definiert sind, mit der Ausnahme, daß alle Reste R^1 bis R^3 gegebenenfalls substituierte aliphatische Reste darstellen können,

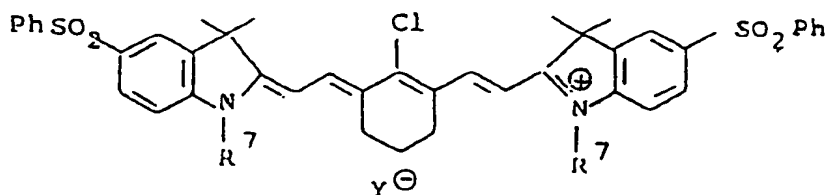


in der R^1 bis R^3 wie oben definiert sind, mit der Ausnahme, daß alle Reste R^1 bis R^3 gegebenenfalls substituierte aliphatische Reste darstellen können, und ein Polymer, enthaltend monomere Einheiten der Formel

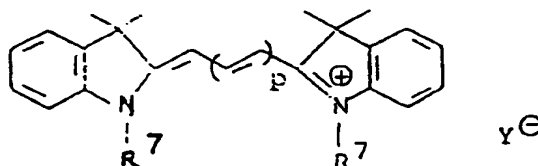


in der X^{\ominus} ein Anion ist.

2. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Harz ein Novolakharz ist und das Oniumsalz in einer Menge von 1 bis 40 Gew.-% des Gesamtgewichtes des phenolischen Harzes und des Oniumsalzes vorhanden ist.
3. Zusammensetzung nach Anspruch 1, dadurch gekennzeichnet, daß das Harz ein Resolharz ist und das Oniumsalz in einer Menge von 5 bis 40 Gew.-% des Gesamtgewichtes des phenolischen Harzes und des Oniumsalzes vorhanden ist.
4. Zusammensetzung nach einem der vorstehenden Ansprüche, dadurch gekennzeichnet, daß das Anion ein Halogenid, HSO_4^{\ominus} , $\text{R}^3\text{CO}_2^{\ominus}$, worin R^3 einen gegebenenfalls substituierten Alkyl- oder Phenylrest darstellt, oder ein Halogen-enthaltendes Komplexion ist.
5. Zusammensetzung nach irgendeinem der vorstehenden Ansprüche, die zusätzlich einen Spektralsensibilisator in einer Menge von bis zu 10 Gew.-% des Gesamtgewichtes von phenolischem Harz, Oniumsalz und Spektralsensibilisator umfaßt.
6. Zusammensetzung nach Anspruch 5, dadurch gekennzeichnet, daß der Spektralsensibilisator aus einer der folgenden Klassen ausgewählt ist: Diphenylmethan-, Xanthen-, Acridin-, Methin- und Polymethin- (einschließlich Oxonol-, Cyanin- und Merocyanin-)farbstoff, Thiazol, Thiazin, Azin, Aminoketon, Porphyrin, gefärbter aromatischer polycyclischer Kohlenwasserstoff, p-substituierte Aminostyrylverbindung, Aminotriazylmethan, Polyarylen, Polyarylpolyen, 2,5-Diphenylisobenzofuran, 2,5-Diarylcylopentadien, Diarylfuran, Diarylthiofuran, Diarylpyrrol, Polyarylphenylen, Coumarin und Polyaryl-2-pyrazolin.
7. Zusammensetzung nach den Ansprüchen 6 oder 7, dadurch gekennzeichnet, daß der Spektralsensibilisator die Formel:



oder



aufweist, in der:

R⁷ einen Alkylrest von 1 bis 6 Kohlenstoffatomen darstellt,Y^o 4-Perfluorethylcyclohexylsulfonat oder ClO₄^o darstellt, und

p 1 oder 2 ist.

8. Zusammensetzung nach einem der vorstehenden Ansprüche, die zusätzlich ein Amin in einer Menge von bis zu 25 Gew.-% des Gesamtgewichtes von phenolischem Harz, Oniumsalz und Amin umfaßt.
9. Zusammensetzung nach Anspruch 8, dadurch gekennzeichnet, daß das molare Verhältnis von Amin zu Oniumsalz ungefähr 1:1 ist.
10. Zusammensetzung nach Anspruch 8 oder Anspruch 9, dadurch gekennzeichnet, daß das Amin Tri-n-butylamin oder Bis(4-dimethylaminophenyl)methan ist.
11. Strahlungsempfindliches Element, umfassend eine auf ein Substrat aufgetragene Schicht der Zusammensetzung nach einem der vorstehenden Ansprüche.
12. Element nach Anspruch 11, dadurch gekennzeichnet, daß das Substrat Papier, Aluminium, Kupfer, eine epoxybeschichtete Kupferplatte, eine Polyesterfolie oder Siliciumdioxid ist.
13. Verfahren zur Herstellung eines lithographischen Bildes auf einem Element nach Anspruch 11 oder Anspruch 12, umfassend:
bildweise Belichtung des Elements mit aktinischer Strahlung, und
Entwicklung der Platte mit einem auf Alkali basierenden Entwickler, so daß die Zusammensetzung von den bestrahlten Bereichen entfernt wird und dadurch das Bild hergestellt wird.
14. Verfahren zur Herstellung eines lithographischen Bildes auf einem Element nach Anspruch 11 oder Anspruch 12, umfassend:
bildweise Belichtung des Elements mit aktinischer Strahlung, Erhitzen des Elements zur Umwandlung der Beschichtung in den bestrahlten Bereichen in eine für Alkali unlösliche Form,
weitere Gesamtbelichtung des Elements mit aktinischer Strahlung, so daß die zuvor nicht-belichteten Bereiche Alkali-löslich gemacht werden, und
Entwicklung des Elements mit einem auf Alkali basierenden Entwickler, so daß die Beschichtung von solchen Bereichen des Elements entfernt wird, die durch die weitere Belichtung löslich gemacht wurden, und dadurch das Bild hergestellt wird.
15. Verfahren nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß der Entwickler wäßriges Natriummetasilikat ist.

FIG. 1

